

Supporting Information

A dumbbell-like A-D-A molecule for single-component organic solar cells

Jiamin Cao, Xiaoyan Du, Shan Chen, Zuo Xiao* and Liming Ding*

*National Center for Nanoscience and Technology, Beijing 100190, China; E-mail:
opv.china@yahoo.com, xiaoz@nanoctr.cn*

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1. General characterization

NMR spectra were measured with a Bruker Avance-400 spectrometer. MALDI-TOF mass spectrum was measured on an Autoflex III spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Thermogravimetric analysis (TGA) was done by a Perkin-Elmer Diamond TG/DTA thermal analyzer. Cyclic voltammetry (CV) was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer. All measurements were carried out in a one-compartment cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ reference electrode. Measurements were performed in ODCB/CH₃CN (9:1) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte at 25 °C (scan rate 0.1 V/s). All potentials were corrected against Fc/Fc⁺. AFM was done on a Dimension 3100 microscope (Veeco).

2. Device fabrication and measurements

Solar cells

Patterned ITO glass with a sheet resistance of 15 Ω sq⁻¹ was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT:PSS, Clevios™ P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 140 °C for 10 min. Triad **1** in chlorobenzene (15 mg/mL) was spin-coated onto PEDOT:PSS layer (1000 rpm for 60 s). Then the films were annealed at 110 °C for 10 min. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10⁻⁴ Pa). The effective area for the devices is 4 mm². *J-V* curves were measured with a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, 91159A, AM 1.5G, 100 mW/cm²). Solar simulator illumination intensity was determined using a

monocrystalline silicon cell (Oriel 91150, 2 × 2 cm) calibrated by NREL. The external quantum efficiency (EQE) and internal quantum efficiency (IQE) spectra were measured using a QE-R3011 measurement system (Enli Technology, Inc.). The thicknesses of the active layers (~60 nm) were measured by a KLA Tencor D-120 profilometer.

Electron-only devices

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was firstly evaporated onto a glass substrate. Triad **1** in chlorobenzene (15 mg/mL) was spin-coated onto Al (1000 rpm for 60 s). Then the films were annealed at 110 °C for 10 min. Ca (~5 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter in the dark.

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 140 °C for 10 min. Triad **1** in chlorobenzene (15 mg/mL) was spin-coated onto PEDOT:PSS layer (1000 rpm for 60 s). Then the films were annealed at 110 °C for 10 min. Finally, MoO₃ (~5 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter in the dark.

3. Synthetic procedures and spectral data

All reagents were purchased from Alfa Aesar Co., Aladdin Co., Acros Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 4,7-Dibromo-2,1,3-benzothiadiazole and

2,6-bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole (DTS) were synthesized according to literatures.¹⁻²

4-(7-Bromobenzo[*c*][1,2,5]thiadiazol-4-yl)but-3-yn-1-ol (3). To a solution of but-3-yn-1-ol (0.05 g, 0.71 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.21 g, 0.71 mmol) in toluene (50 mL) and triethylamine (35 mL) were added CuI (40 mg, 0.21 mmol) and Pd(PPh₃)₂Cl₂ (100 mg, 0.14 mmol) under argon. The mixture was stirred vigorously at 65 °C for 48 h, and then cooled to room temperature. After removal of the solvent, the crude product was purified through a silica gel column with dichloromethane to give a gray white solid (105 mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.79 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 3.92 (br, 2H), 2.84 (t, *J* = 6.1 Hz, 2H), 2.20 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.60, 152.95, 132.49, 131.88, 116.69, 114.34, 95.27, 77.98, 60.86, 24.30.

4,4'-(7,7'-(4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-*b*:4,5-*b'*])dithiophene-2,6-diyl)bis(benzo[*c*][1,2,5]thiadiazole-7,4-diyl))bis(but-3-yn-1-ol) (2). To a solution of compound **3** (0.29 g, 1.0 mmol) and DTS (0.37 g, 0.5 mmol) in toluene (50 mL) was added Pd(PPh₃)₄ (60 mg, 0.05 mmol) under argon. The mixture was heated to reflux for 24 h, and then cooled to room temperature. After removal of the solvent, the crude product was purified through a silica gel column with dichloromethane/ethyl acetate (1:1) to give a purple solid (128 mg, 31%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.23 (t, *J* = 3.4 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 7.1 Hz, 2H), 3.98 (t, *J* = 5.8 Hz, 4H), 2.89 (t, *J* = 5.8 Hz, 4H), 2.48 (br, 2H), 1.62-1.57 (m, 2H), 1.43-1.07 (m, 20H), 0.89-0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.19, 150.99, 150.61, 145.14, 141.11, 132.13, 131.57, 127.28, 123.57, 113.90, 95.18, 78.73, 60.94, 36.11, 35.83, 29.08, 28.98, 24.65, 23.11, 17.84, 14.24, 10.89. MALDI-TOF-MS (+) for C₄₄H₅₀N₄O₂S₄Si [M⁺]: 822.8.

Triad 1. A solution of compound **2** (75 mg, 0.09 mmol) and PCBA (179 mg, 0.2 mmol) in dichlorobenzene (20 mL) was sonicated for 1 h. After being cooled to 0 °C,

N,N'-dicyclohexylcarbodiimide (DCC) (150 mg, 0.72 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, 0.72 mmol) were added. The mixture was stirred at 25 °C overnight. After removal of the solvent, the crude product was purified through a silica gel column with dichloromethane to give a purple solid (125 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (m, *J* = 5.1 Hz, 2H), 7.90 (d, *J* = 7.3 Hz, 4H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 4H), 7.46 (t, *J* = 7.3 Hz, 2H), 4.39 (t, *J* = 6.4 Hz, 4H), 2.97-2.91 (m, 8H), 2.61 (t, *J* = 7.2 Hz, 4H), 2.26-2.19 (m, 4H), 1.54-1.49 (m, 2H), 1.36-1.02 (m, 20H), 0.82-0.79 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.76, 155.51, 151.65, 150.78, 148.67, 147.63, 145.63, 145.17, 145.10, 145.06, 144.95, 144.89, 144.70, 144.58, 144.41, 144.31, 143.92, 143.67, 143.02, 142.90, 142.84, 142.80, 142.10, 142.08, 142.04, 142.02, 140.86, 140.79, 140.64, 137.92, 137.48, 136.69, 133.24, 132.05, 131.43, 128.40, 128.22, 127.95, 124.22, 114.52, 93.15, 79.81, 78.52, 62.13, 51.82, 36.01, 35.78, 34.10, 33.59, 29.00, 28.94, 23.07, 22.43, 20.64, 17.71, 14.25, 10.88. MALDI-TOF-MS (+) for C₁₈₆H₇₀N₄O₄S₄Si [M⁺]: 2580.7.

4. NMR spectra

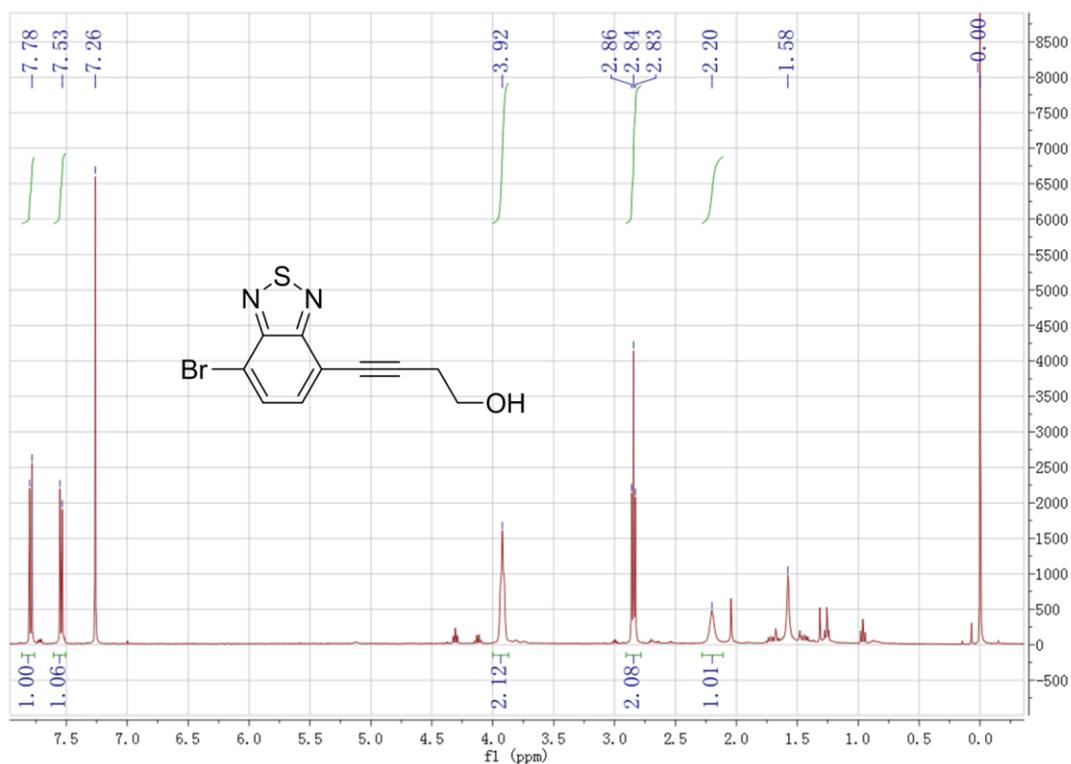


Fig. S1 ¹H NMR spectrum of compound 3.

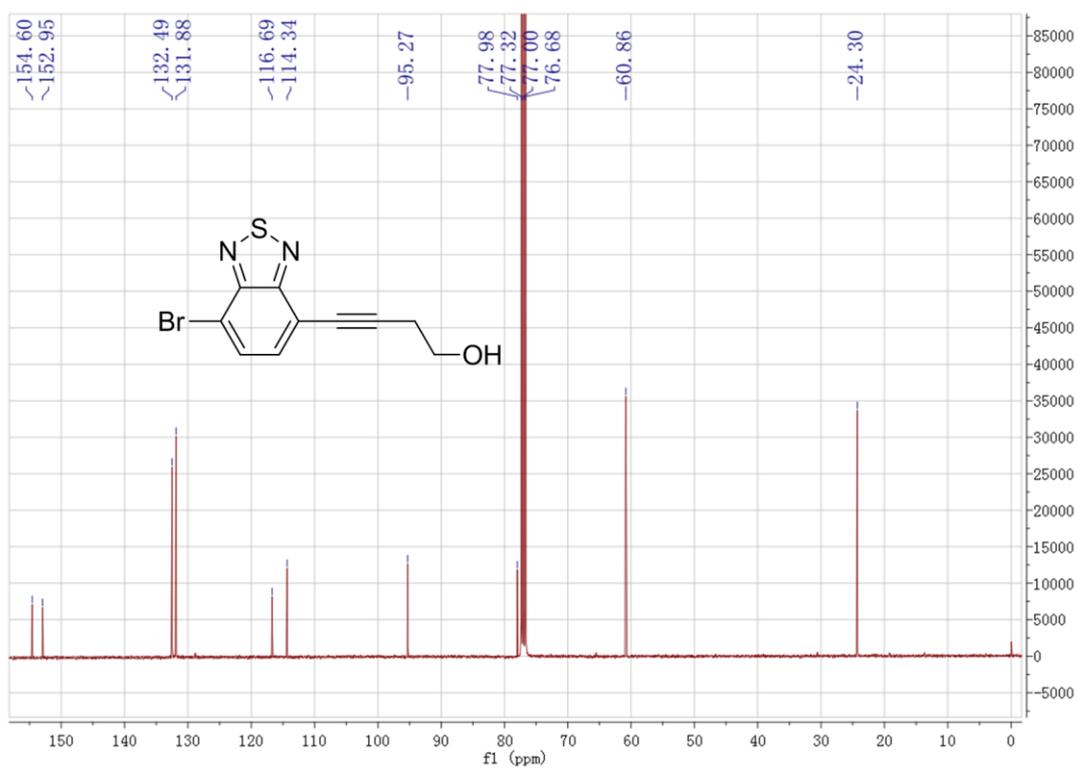


Fig. S2 ¹³C NMR spectrum of compound 3.

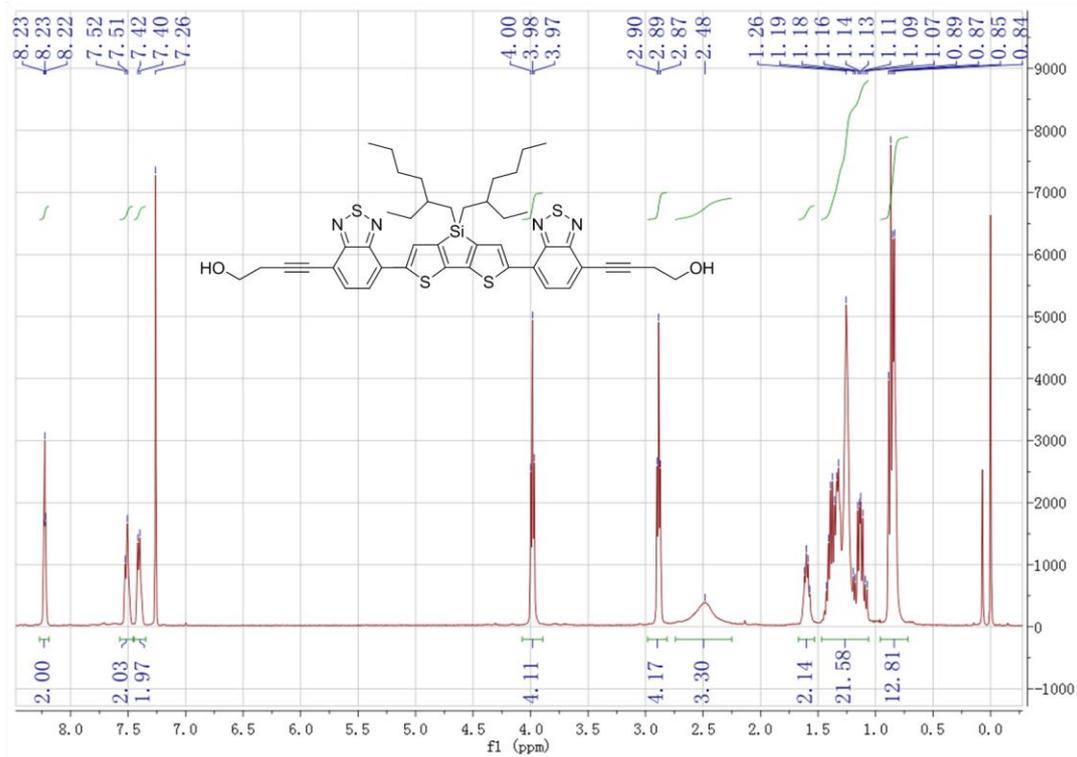


Fig. S3 ¹H NMR spectrum of compound **2**.

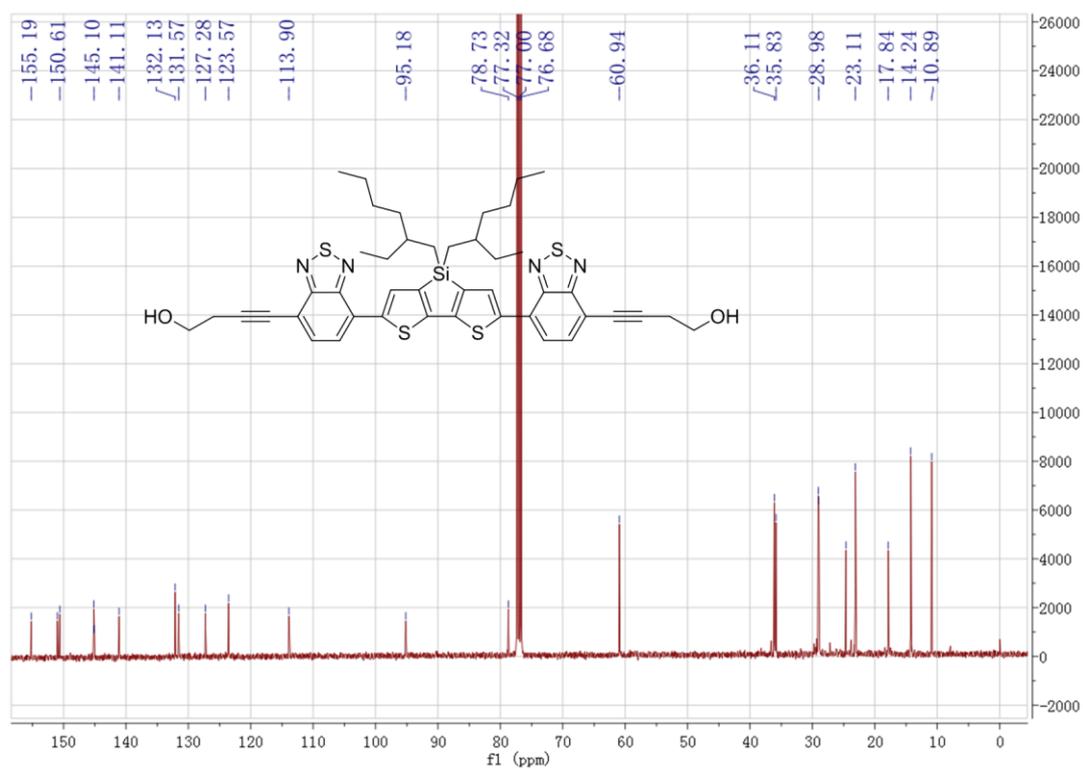


Fig. S4 ¹³C NMR spectrum of compound **2**.

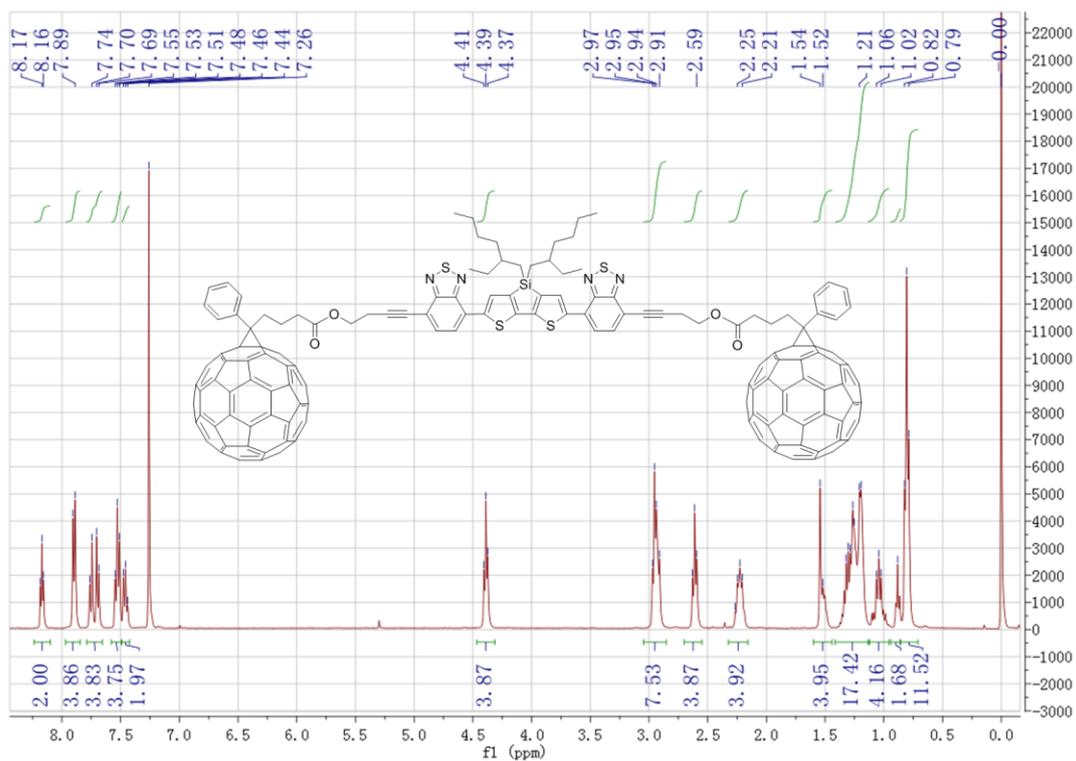


Fig. S5 ^1H NMR spectrum of triad 1.

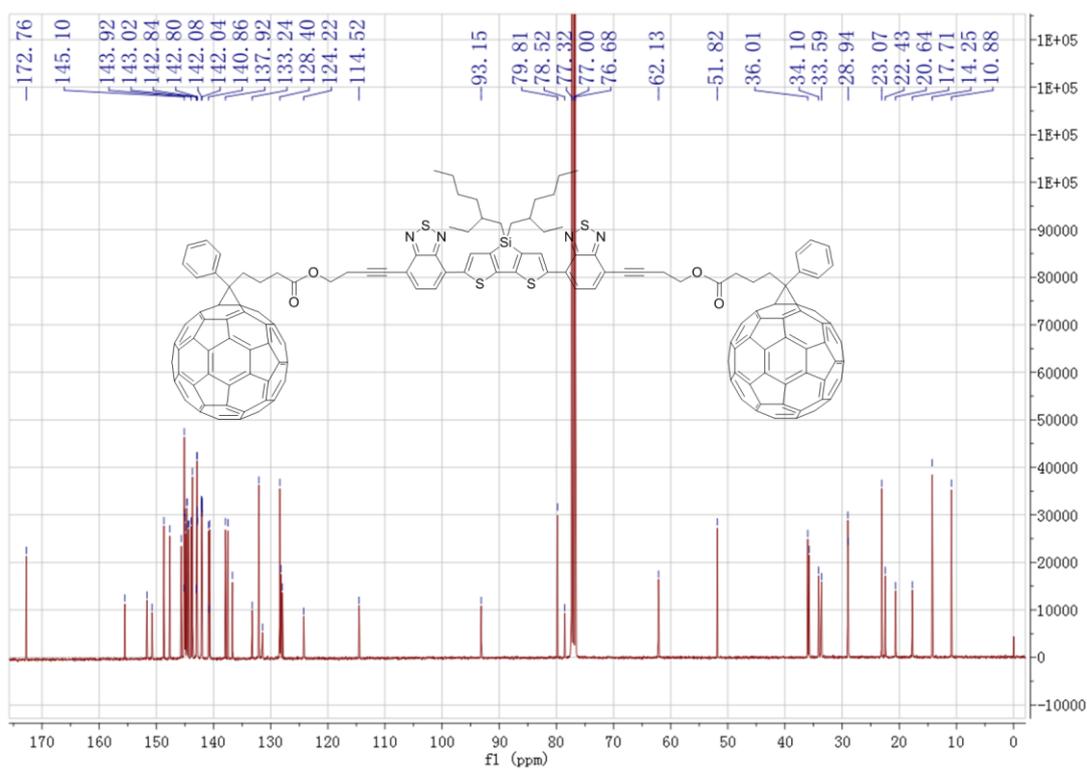


Fig. S6 ^{13}C NMR spectrum of triad 1.

5. Mass spectrum

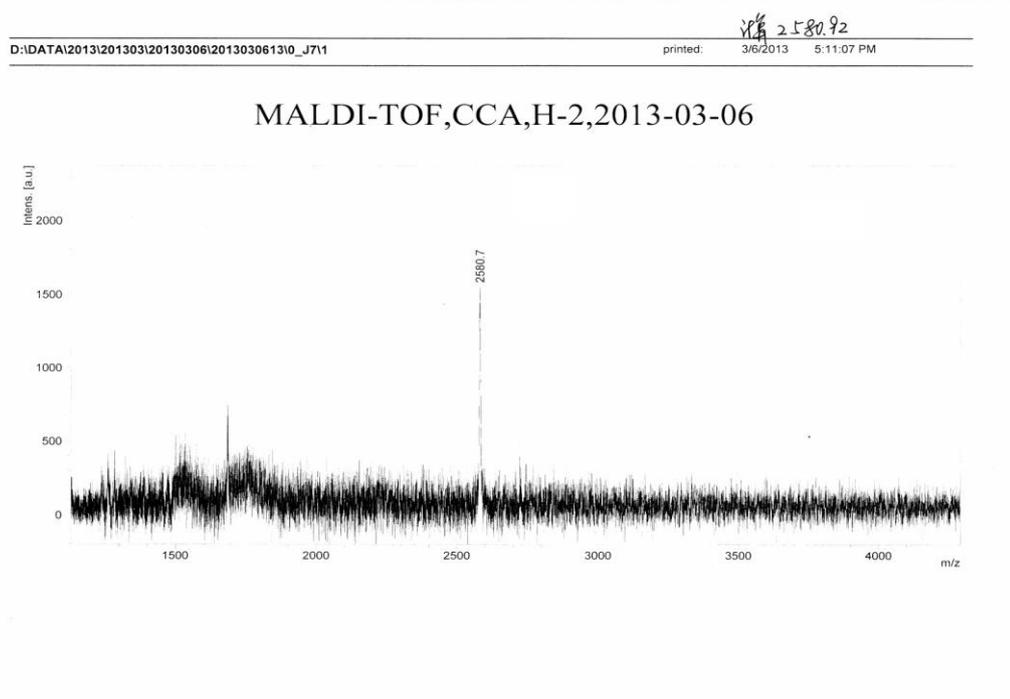


Fig. S7 Mass spectrum of triad **1**.

6. TGA

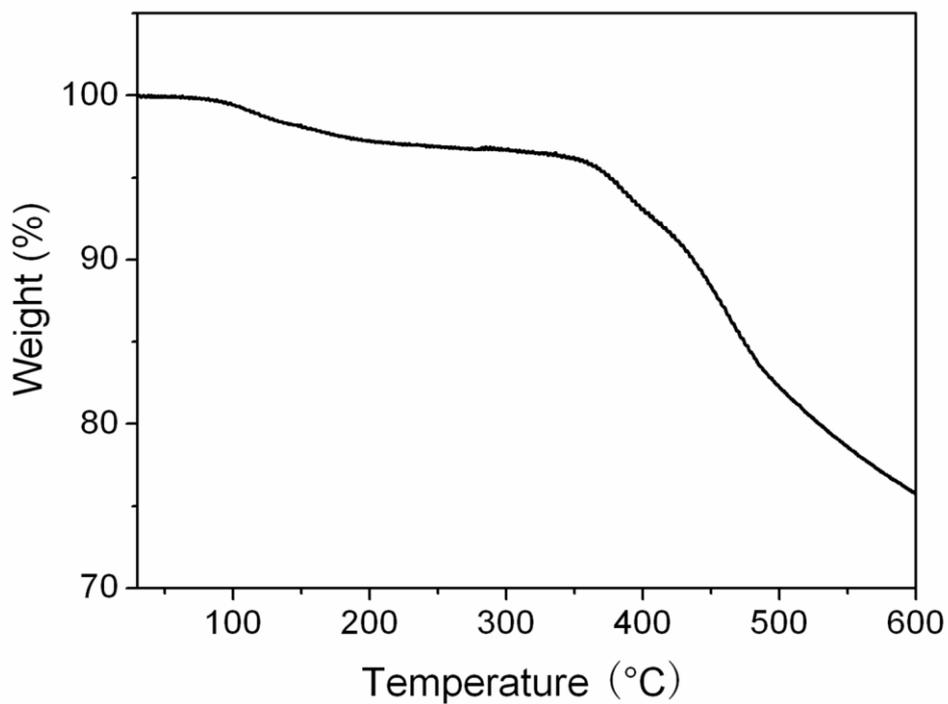


Fig. S8 TGA curve of triad **1**.

7. Space charge limited current (SCLC) measurements

The charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility for electrons (μ_e) or holes (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the film thickness, and V is the effective voltage, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential which results from workfunction difference for anode and cathode. Figure S9 (a) shows J - V curves of the electron-only and hole-only devices. The mobility was calculated from the slope of $J^{1/2}$ - V curves.

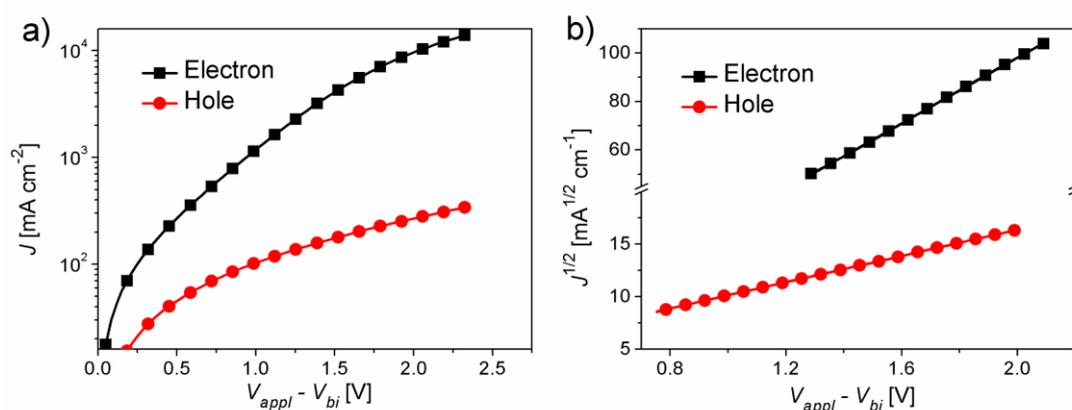


Fig. S9 J - V curves (a) and the corresponding $J^{1/2}$ - V curves (b) for electron-only or hole-only devices (in dark). The thicknesses of the films are 60 nm and 65 nm, respectively.

8. AFM

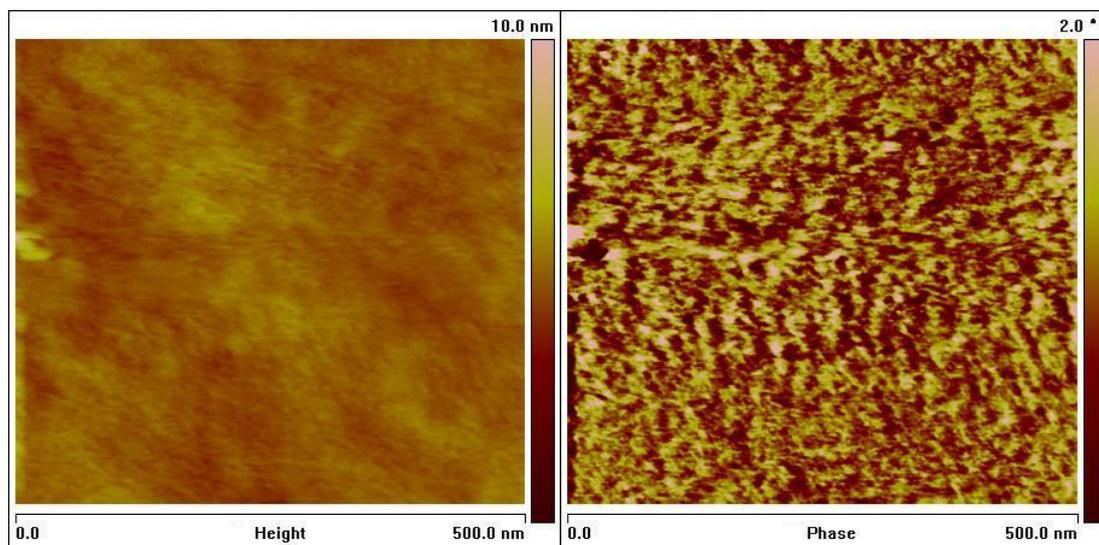


Fig. S10 AFM images for triad **1** film.

References

- [1] J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012.
- [2] J. Cao, W. Zhang, Z. Xiao, L. Liao, W. Zhu, Q. Zuo and L. Ding, *Macromolecules*, 2012, **45**, 1710.